Available online at www.sciencedirect.com

ScienceDirect

Procedia Structural Integrity 2 (2016) 104–111

Structural Integrity Procedia

www.elsevier.com/locate/procedia

21st European Conference on Fracture, ECF21, 20-24 June 2016, Catania, Italy

Toughening and Mechanical Properties of Epoxy Modified with Block Co-polymers and MWCNTs

Ankur Bajpai, Arun Kumar Alapati, Bernd Wetzel*

Institut für Verbundwerkstoffe GmbH (IVW), Technical University of Kaiserslautern,
67633 Kaiserslautern, Germany
http://www.ivw.uni-kl.de/

Abstract

The objective of this work was to systematically develop and understand novel polymeric hybrid nanocomposites that include block copolymers (BCP) with tailored morphologies in order to generate high toughness. Furthermore, rigid fillers in the form of multi-walled carbon nanotubes (MWCNT) were added systematically together with block copolymers to study the combined effect of rigid nanofillers and more ductile BCP particles. The resulting matrix was extensively and carefully characterized by standard methods. This included thorough characterization of mechanical, fracture mechanical and thermal properties. Results show that both fracture toughness, K_{Ic}, and critical energy release rate, G_{Ic}, were increased linearly to a maximum of 2.10 MPa.m$^{1/2}$ and 1.46 kJ/m^2 respectively by the addition of 12 wt. % BCP. Fractography studies reveal toughening mechanisms of the nanocomposites that were identified as both the cavitation of spherical micelles and enhanced plastic deformation and furthermore fiber pull-out in the case of hybrid nanocomposites.

Peer-review under responsibility of the Scientific Committee of ECF21.

Keywords: Thermosets; Epoxy; Block Copolymers; CNT's; Mechanical properties; Fracture Toughness;

* Corresponding author. Tel.: +49-(0)631-2017-119 ; fax: +49-(0)631-2017-199 .
E-mail address: bernd.wetzel@ivw.uni-kl.de

Copyright © 2016 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).
Peer review under responsibility of the Scientific Committee of ECF21.
10.1016/j.prostr.2016.06.014

1. Introduction

Epoxy resin systems are a class of high-performance thermosets commonly used as a matrix in a wide range of automotive, electronics, and aerospace applications. Such wide range of applications is achieved by selecting a proper epoxy resin and curing agent which is further processed in a felicitous curing schedule. Properties like high modulus, high strength, and good thermal and dimensional stability make it popular in composite applications (Petrie, 2006).The mechanical properties of epoxy matrices can further be altered and improved by adjusting the molecular structure and architecture, e.g. by increasing the crosslink density to produce high stiffness and strength (Sue, et al., 2000).

The incorporation of ductile organic and hard inorganic micro- and nano-particulate fillers is a well-known pathway to improve mechanical properties, and in particular toughness, of brittle thermosetting polymers such as epoxy resins. To overcome brittleness, reactive rubber modifiers, e.g. carboxy-terminated butadiene acrylonitrile (CTBN) can react into the epoxy which increases its toughness but with the sacrifice of strength and thermal properties (Liang & Pearson, 2010). Also, core-shell particles, typically a PMMA shell surrounding a low T_g rubber core or thermoplastic spheres such as polysulfone (PSU) can increase toughness, but they need to be homogeneously distributed in the matrix to become effective (Jorg, et al., 2004) (Pearson & Yee, 1993). Especially ceramic fillers with nano-dimension, e.g. alumina and silica have proven their ability to increase fracture toughness, and furthermore to reinforce also mechanical properties such as modulus of elasticity and strength while only marginally restricting polymer ductility at low nanofiller concentrations. Indeed, nanofillers attain a significant improvement in rigidity and reinforcement of epoxy already at rather low filler contents (Wetzel, et al., 2002) (Wetzel, et al., 2003) (Wetzel, et al., 2006). However, one of the main drawbacks is the presence of particle agglomerates in commercially available gas phase synthesized ceramic nanoparticle powders. The occurrence of agglomerates in a brittle polymer must be avoided because they act as flaws and generate local stress peaks which reduce strength, ductility, and fracture toughness of the polymer. For manufacturing such nanocomposites costly mechanical dispersion techniques are usually undertaken in order to homogeneously distribute nanoparticles as individuals within the resin.

For avoiding mechanical dispersion efforts an innovative approach creates further potential to realize varying nanostructures with both stiff and ductile building blocks by using a new class of block-copolymers (BCP) (Robert, et al., 2008). A new family of block copolymers (Nanostrength, Arkema) has the ability to self-assemble on the nanoscale. Various nanophase morphologies can be realized that are well-integrated into the polymer matrix. They are constituted of three blocks of linear chains covalently bonded to one another either by MAM (Fig. 1.a) and/or functional MAM (Fig. 1.b) (Arkema Inc., Paris, France, 2013). MAM are constituted of pure acrylic symmetric block copolymers with a centre block of poly (butyl acrylate) and two side blocks of poly (methyl methacrylate). In functional MAM, the two side blocks contain specific functionalities to enhance their miscibility with a wide range of thermosetting systems, because of repulsive interactions between the three blocks.

Figure 1.a Poly[(methyl)methacrylate] -b- poly(butyl acrylate) -b- poly[(methyl)methacrylate]

Figure 1.b Poly[(methyl)methacrylate-co-polar comonomer] -b- poly(butyl acrylate) -b-poly[(methyl)methacrylate- co-polar comonomer]

Nano-structuration is induced by strong repulsive forces between the side and middle blocks and is primarily governed by thermodynamics and thus independent of processing conditions. Controlling factors are the polarity of building blocks, miscibility, and concentration which allows to adjust various morphologies, e.g. spherical nanoparticles, vesicles, and micelles with network-like structure (Robert, et al., 2008) (Arkema Inc., Paris, France, 2013). By further incorporating MWCNTs in formulations containing spherical silica or rubber particles superior electrical conductivity with balanced stiffness, strength, fracture toughness and T_g are obtained (Long-Cheng, et al., 2013). Multi-walled carbon nanotubes (MWCNTs) have a much larger diameter and exhibit better dispersibility in polymer suspensions due to the lower specific surface area than single-walled carbon nanotubes (SWCNTs). Previous studies show that amino functionalization in CNTs improves the dispersibility and interfacial adhesion in the epoxy matrix over some other functionalizations such as carboxyl or silane (Ma, et al., 2010).

2. Experimental

The materials in this study were a standard Bisphenol-F epoxy resin (EPON 862 by Hexion) cured by an aromatic diamine curing agent (Ethacure 100 by Albemarle) and a functionalized PMMA-*bloc*-PbuA-*bloc*-PMMA copolymer. The MAMs are built up of symmetrically arranged diblock BCPs with one stiff PMMA block which is connected by a more ductile PBuA block (Nanostrength D51N, Arkema). When MAM block copolymers are dispersed in the DGEBF resin system, they self-assemble into the thermosetting network during reaction induced phase separation. Thereby epoxy-miscible PMMA blocks provide affinity to the epoxy monomers while the PBuA blocks are an epoxy-non-miscible soft rubber phase and separate as the second phase.

The BCP concentration was varied systematically from 0 to 12 wt. %. For hybrid nanocomposites multi-walled carbon nanotubes (MWCNT, Arkema, type Graphistrength C S1-25) were used as rigid fillers. The MWCNT are provided in the form of dry granules made from epoxy which contain 25 wt. % MWCNT. The interfacial area may influence the properties of nanocomposites, so it is necessary to ensure the proper distribution of MWCNTs and to avoid agglomerates in the epoxy resin. Therefore, the epoxy/MWCNT granules were firstly dispersed in the liquid epoxy matrix polymer in order to produce a masterbatch from which a series of nanocomposites was subsequently manufactured. The granules containing the MWCNT were immersed in the base resin in an oven overnight at a temperature of 80°C and then stirred by an impeller at 500 rpm for 2 hours. This mixture was then dispersed using a three roll calendar (TRC) mill (Exakt 80E, EXAKT Vertriebs GmbH &Co., Germany) to produce a masterbatch which contains 1wt. % MWCNTs. The dispersion quality of MWCNT was controlled after each pass using a North bar (Fig. 2.b) until no agglomerates were found (Arkema Inc, 2012).

Preparation of BCP nanocomposites takes fewer efforts compared to those containing MWCNT's. Firstly, the required amount of BCP was mixed gently with preheated DGEBF and the mixture was dispersed in a dissolver (Dispermat, Getzmann GmbH) at 90°C until the transparent mixture was obtained ensuring complete melting of BCP in the epoxy. After that, the modified epoxy was cooled down to 55°C and mixed with a stoichiometric amount of curing agent by stirring for 5-10 min at 350 rpm. For preparing hybrid mixtures the masterbatch containing MWCNT (1 wt. %) was thinned down and stirred at 350 rpm for 50 min at 80°C while removing entrapped air by vacuum. Then, the calculated amount of BCP was added and mixed for 30 min at 350 rpm. Finally, the stoichiometric amount of curing agent was added and the mixture was stirred thoroughly for 5-10 min at 350 rpm. The mixture was then cast into glass molds to produce tensile samples and into steel molds for compact tension (CT) specimens, respectively. The samples were cured in two steps at 80°C for 8 hours and at 120°C for 18 hours.

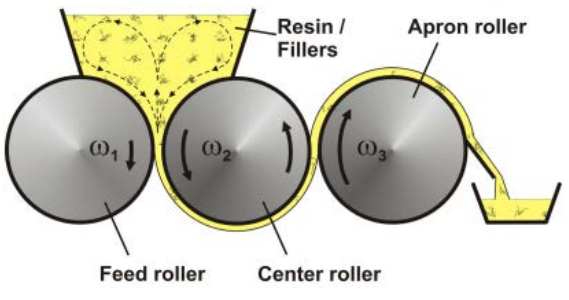

Figure 2.a Schematic view of TRC

Figure 2.b Dispersion control by North bar

Mechanical properties of the cured nanocomposites were determined by static and dynamic testing methods. Tensile testing was performed using dog-bone shaped specimens according to DIN EN ISO 527-1 and a Zwick universal testing machine at room temperature. The testing speed was set to 2 mm/min. For each specimen at least five samples were tested. Differential scanning calorimetry (DSC) was performed on a Mettler Toledo equipment (DSC1 Star system) to determine glass transition temperature. The samples were heated from room temperature up to 200 °C and

then cooled down to room temperature, and then followed by a second heating cycle to 200 °C at a heating rate of 10 K/min.

Linear elastic fracture mechanics (LEFM) allows measuring the intrinsic fracture toughness of brittle solids (Moore, 2004). Independent of the specimen geometry the LEFM provides information about the initiation of cracks in epoxy nanocomposites. The static fracture toughness was determined by means of compact tension (CT) tests on at least five specimens according to ISO 13586 standard using a Zwick universal testing machine at room temperature and at low deformation speeds of 0.2 mm/min. The thickness B and the width W of specimens were chosen to be 6 mm and 36 mm, respectively. Prior to testing, a notch was machined and then sharpened by tapping a fresh razor blade into the material, so that a sharp crack was initiated with a length a_0 between 0.45*W and 0.55*W. The fracture toughness K_{Ic} was then calculated by Eq. (1), where F is the maximum force observed in the load-displacement curve, and a_0 is the initial crack length for calculating $\alpha = a/W$ and $f(a/W)$ as follows:

$$K_{IC} = \frac{F}{B\sqrt{W}} . f(a/W) \tag{1}$$

$$f\left(\frac{a}{W}\right) = f(\alpha) = \frac{(2+\alpha)}{(1-\alpha)^{3/2}} . (0.866 + 4.64\alpha - 13.32\alpha^2 + 14.72\alpha^3 - 5.60\alpha^4) \tag{2}$$

The knowledge of the critical stress intensity factor K_{Ic}, the elastic modulus E_t, and the Poisson's ratio ν(~0.35) allows calculating the critical energy release rate G_{Ic}:

$$G_{Ic} = \frac{K_{Ic}^2(1 - \upsilon^2)}{E_t} \tag{3}$$

Information about toughening mechanisms in the nanocomposites were studied with the help of a field emission scanning electron microscope (SEM SUPRA™ 40 VP, Carl Zeiss NTS GmbH, Germany). Before scanning, the surfaces of the samples were sputtered with a thin layer of gold and palladium using a sputtering device (SCD-050, Balzers, Liechtenstein).

3. Results and Discussions

3.1 Glass Transition Temperature

The T_g of the unmodified epoxy was measured to be 141 °C. The values of T_g were reduced by the addition of the MAM block copolymers, see Table 1, although the reduction of T_g was small. The PMMA fraction and the better compatibility of the PMMA with epoxy is expected to lead to a plasticization effect in the D51N modified epoxies since more PMMA with low T_g (about 100 °C) (Biron, 2007) (Fried, 2003) remains dissolved in the epoxy matrix. This explains the lower T_g measured for the D51N modified epoxies. At lower concentration the T_g of the MWCNTs modified epoxies decreases with increase in their concentration. The addition of CNTs into epoxy decreases the overall degree of cure compared to neat epoxy under the same curing conditions, which is possibly due to the steric hindrance of CNTs impacting the mobility of the monomers and a curing agent. As a result, the glass transition temperature of the epoxy/MWCNT nanocomposites is usually lower than neat epoxy (Kun, et al., 2006) (Joonwon, et al., 2002).

3.2 Tensile Behaviour of the Composites

The values of the elastic modulus, the tensile strength, and the strain a maximum stress of the MAM modified epoxy polymers are shown in Table 1. A tensile modulus of 2950 MPa and a tensile strength of 84 MPa were measured for the unmodified epoxy. The addition of MAM led to a decrease in the tensile modulus and strength, which was expected because the D51N block copolymers are softer than the epoxy and moreover, it contains the softer phase content in the medium range (Arkema Inc., Paris, France, 2013). This is clearly demonstrated for 12 wt. % of D51N where modulus and strength are reduced to 2670 MPa and 76.2 MPa, respectively. The addition of the MAM particles reduced the modulus nearly linearly with increasing content, but up to a content of 4 wt. % the tensile strength even slightly increased or remained at the level of the neat epoxy. By adding MWCNTs, tensile properties increased with

MWCNT content by ca. 5% in case of nanocomposites containing 0.075 wt. % MWCNT. Results show that in the case of hybrid nanocomposites (D51N+MWCNT) modulus, strength and strain at yield tend to decrease with the increase of MAM particle concentration.

Table 1: Mechanical, fracture mechanical and thermal properties of different nanocomposites formulations

***D51N* [wt%]** (vol. %)	E_t [MPa]	σ_m [MPa]	ε_m [%]	K_{Ic} [MPa.m$^{1/2}$]	G_{Ic} [kJ/m²]	T_g [°C]
0%	2950 (±75.8)	84 (±0.7)	6.3 (±0.4)	0.57 (±0.04)	0.096 (±0.03)	141.0
2% (1.7%)	2920 (±18.7)	86 (±0.3)	6.8 (±0.4)	1.34 (±0.19)	0.540 (±0.18)	139.4
4% (3.5%)	2890 (±19.6)	84.5 (±0.3)	6.6 (±0.3)	1.54 (±0.03)	0.720 (±0.03)	140.2
6% (5.2%)	2850 (±14.8)	82 (±0.2)	6.2 (±0.5)	1.76 (±0.37)	0.960 (±0.47)	135.5
8% (7%)	2750 (±25.3)	79.6 (±0.6)	6.2 (±0.6)	1.94 (±0.22)	1.210 (±0.24)	136.5
10% (8.6%)	2690 (±47.5)	78.4 (±0.7)	6.1 (±0.5)	2.01 (±0.12)	1.320 (±0.16)	134.7
12% (10.4%)	2670 (±15.6)	76.2 (±1)	5.8 (±0.6)	2.10 (±0.29)	1.460 (±0.44)	137.4
***MWCNT* [wt%]** (vol. %)	E_t [MPa]	σ_m [MPa]	ε_m [%]	K_{Ic} [MPa.m$^{1/2}$]	G_{Ic} [kJ/m²]	T_g [°C]
0.05% (0.042%)	2860 (±34.4)	85.2 (±0.8)	5.9 (±0.8)	1.05 (±0.23)	0.34 (±0.14)	136.7
0.075% (0.062%)	3060 (±31.7)	88.5 (±0.8)	6.1 (±1.6)	1.13 (±0.07)	0.36 (±0.04)	134.3
0.1% (0.083%)	2960 (±24.7)	75.9 (±0.7)	3.9 (±0.7)	1.33 (±0.20)	0.53 (±0.15)	140.0
***D51N* + *MWCNT* [wt%]** (vol. %)	E_t [MPa]	σ_m [MPa]	ε_m [%]	K_{Ic} [MPa.m$^{1/2}$]	G_{Ic} [kJ/m²]	T_g [°C]
2% + 0.075% (1.7% + 0.062%)	2820 (±65.3)	74.0 (±2.0)	3.9 (±0.1)	1.23 (±0.28)	0.50 (±0.26)	134.9
4% + 0.075% (3.5% + 0.062%)	3020 (±42.4)	74.9 (±3.1)	3.7 (±0.3)	1.33 (±0.13)	0.52 (±0.10)	131.8
6% + 0.075% (5.2% + 0.062%)	2960 (±19.2)	72.7 (±2.9)	3.6 (±0.2)	1.41 (±0.08)	0.59 (±0.06)	136.8

3.3 Fracture Properties

The fracture toughness, K_{Ic}, and fracture energy, G_{Ic}, for the unmodified epoxy, MAM and MWCNTs modified epoxy samples are summarized in Table 1. The values of K_{Ic} and G_{Ic} for the unmodified epoxy were measured as 0.57 MPa.m$^{1/2}$ and 0.096 kJ/m², respectively. The addition of MAM led to a significant improvement in toughness. For D51N modified epoxy, the values of K_{Ic} and G_{Ic} increased strongly with increasing concentration of MAM. The maximum fracture toughness, K_{Ic} of 2.1 MPa.m^{½} and G_{Ic} of 1.46 kJ/m² was measured for 12% D51N. The results are in good agreement with the work of Klingler et al (Klingler, 2013).

Furthermore, the fracture toughness of epoxy resin nanocomposites is increasing with the addition of MWCNTs. For manufacturing hybrid nanocomposites a constant amount of 0.075 wt. % MWCNT was selected, and the content of D51N was systematically varied. Also for the hybrid nanocomposites, an increase in fracture toughness K_{Ic} was

detected. For the material containing 6 wt. % D51N and 0.075 wt. % MWCNT the K_{Ic} was 1.41 MPa.m$^{1/2}$ and the G_{Ic} 0.59 kJ/m^2. The MWCNTs enhanced the toughness of epoxy less efficiently than the BCP.

3.4 Toughening Mechanisms

Visual analysis of the fracture surface using the electron microscope gives an insight on the dispersion state of the particles within the epoxy matrix with cause and location of the failure. The fracture surface of the unmodified epoxy resin exhibits a brittle behavior characterized by the smooth surface area, and only small scale river lines were observed at the crack tip, which was caused by the presence of local mixed mode I/III stresses (Pritchard & Rhoades, 1976).

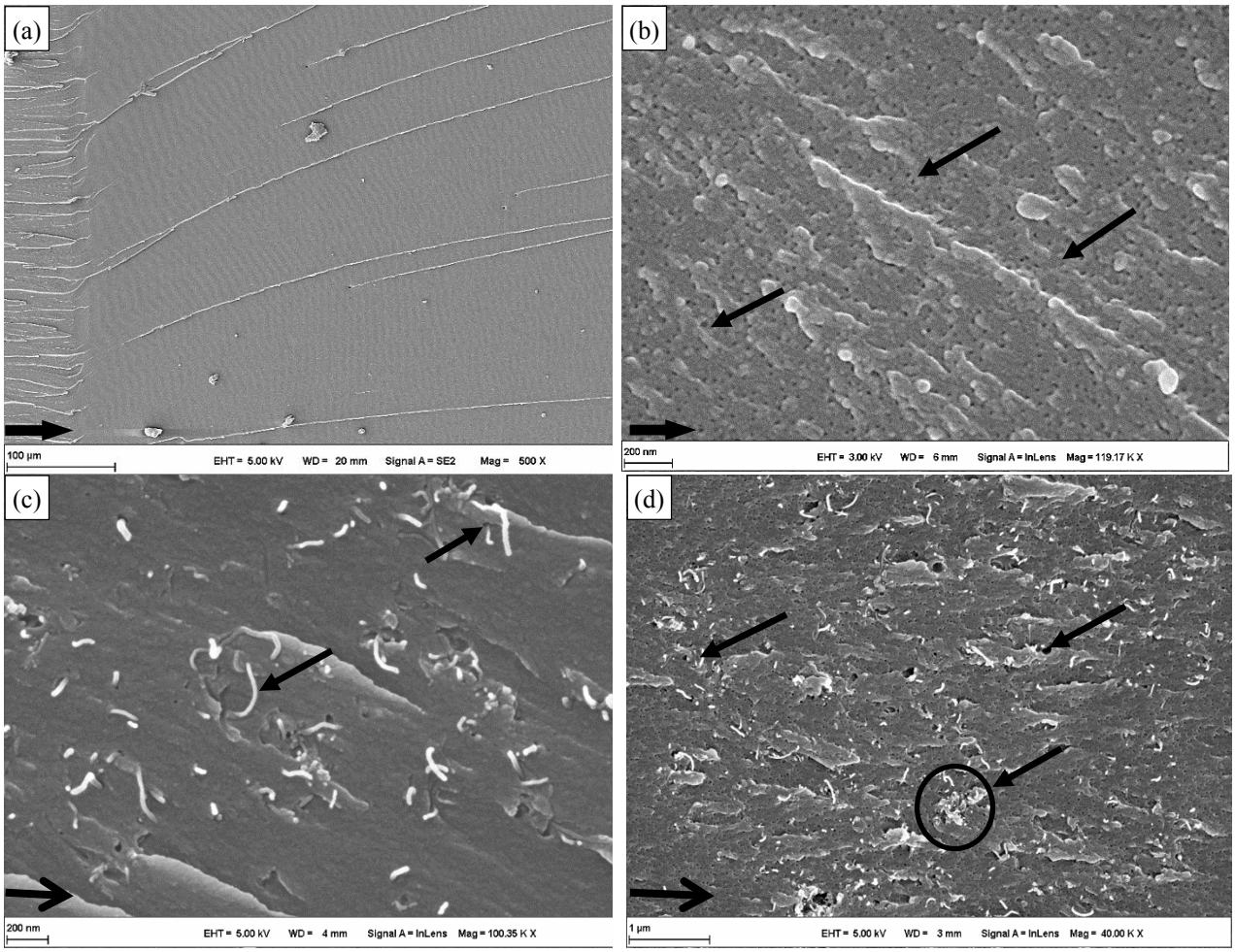

Figure 3: SEM images of fractured surfaces. Crack propagation direction from left to right. (a) Unmodified epoxy, (b) 8 wt. % D51N, (c) 0.075 wt. % MWCNT, (d) 6 wt. % D51N + 0.075 wt. % MWCNT.

The addition of D51N leads to a minor change in the macroscopic appearance of the fracture surface of the nanocomposite structure as shown in Figure 3b. In high magnification SEM micrographs the epoxies containing D51N show small cavities in the dimension of ca. 50 nm as shown in Figure 3b and 3d. Moreover, small-scale matrix tearing was seen on the fracture surfaces of the D51N modified epoxies. These traits indicate the enhanced plastic deformation of the epoxies. Further examination of the fracture surfaces in Figure 3b, reveals that the toughening mechanisms of the modified epoxies are proposed to be cavitation of spherical micelles and the enhanced plastic deformation of the

epoxy matrix due to the localized plasticization effect of the epoxy/PMMA interface. A large number of nano-scale cavities, matrix tearing and multi-planar features on the fracture surfaces of the D51N modified epoxies with spherical micelles, were observed.

Nano-scale cavities and debonded MWCNT nanofibers were identified in the fracture surfaces as shown in Figure 3c. Accordingly, fibre pull-out and debonding is believed to be the dominating toughening mechanisms associated with these MWCNT in epoxy. Since van der Waals forces create a mutual attraction of the MWCNTs they can drive MWCNT assemblage into agglomerates in the epoxy matrix even after proper dispersion processes (Ma, et al., 2010). The presence of agglomerates is known to reduce the material's toughness and ability to resist fracture. Indeed, a few agglomerates of MWCNT were found as shown in fig 3d. This might be a reason, why the addition of the MWCNT has only little effect on the toughening of epoxy. The toughening mechanisms of the hybrid modified epoxies are believed to be the same as those in the D51N and the MWCNTs modified epoxies, which are the cavitation of the D51N spherical micelles, and fibre pull-out of MWCNTs, and the enhanced plastic deformation in the epoxy matrix due to the localized plasticization of the epoxy/PMMA interface.

4. Conclusion

An amine-cured bisphenol-F based epoxy polymer was modified using functionalized poly(methyl methacrylate) block joined with poly(butyl acrylate) MAM diblock copolymers (BCP) supplied by Arkema, France. The microstructure, fracture properties, and toughening mechanisms on the resulting nanocomposites could be identified. The D51N self-assembled into nanoscale spherical micelles, which became increasingly interconnected into a network as the concentration of modifier was increased. The glass transition temperature of unmodified epoxy was affected by the addition of D51N MAM, and the tensile modulus decreased, as expected when incorporating a relatively softer material into epoxy. The critical energy release rate indicated by G_{Ic} was strongly increased to a maximum of 1.46 kJ/m^2 by the addition of 12 wt. % D51N MAM. Compared to the BCP the fracture toughness was much less improved by the addition of MWCNT, and so far no synergistic toughening effects could be found between the D51N and the MWCNT.

Acknowledgment

The authors gratefully acknowledge the provision of the materials by Arkema.

References

Arkema Inc., Paris, France, 2013. Technical Data Sheet- Nanostrength for Epoxies. [Online] Available at: www.nanostrength.com

Arkema Inc, 2012. GRAPHISTRENGT CS 1-25 : PROCESSING GUIDELINE FOR DISPERSION into LIQUID EPOXY., Paris,France: s.n.

Biron, M., 2007. Thermoplastics and Thermoplastic Composites.. Oxford: Elsevier Science Publishers Ltd.

Fried, J. R., 2003. Polymer Science and Technology, 2nd ed.. Upper saddle river: Pearson Education Inc.

H, D. W., P M, A. & Karl, S., 2013. Nanocomposite toughness from a pull-out mechanism. Composites Science and Technology, 83, 27-31.

Joonwon, B., Jyongsik, J. & Seong-Ho, Y., 2002. Cure Behavior of the Liquid-Crystalline Epoxy/Carbon Nanotube System and the Effect of Surface Treatment of Carbon Fillers on Cure Reaction. Macromolecular Chemistry and Physics, 203(15), 2196-2204.

Jorg, F. et al., 2004. Reactive core/shell type hyper branched block copolyethers as new liquid rubbers for epoxy toughening.. Polymer , 45, 2155–2164 .

Klingler, A., 2013. Ermüdungsrissausbreitung in duroplastischen Nanoverbundwerkstoffen, Studienarbeit, Kaiserslautern: Institut für Verbundwerkstoffe GmbH.

Kun, T. et al., 2006. Effects of carbon nanotube fillers on the curing processes of epoxy resin-based composites. Applied Polymer Science, 102(6), 5248-5254.

Liang, Y. L. & Pearson, R. A., 2010. The toughening mechanism in hybrid epoxy-silica-rubber nanocomposites.

Polymer, 51, 4880-4890.
Long-Cheng, T. et al., 2013. Fracture toughness and electrical conductivity of epoxy composites filled with carbon nanotubes and spherical particles. Composites: Part A, 45, 95-101.
Ma, P. C., Mo, S. Y., Tang, B. Z. & Kim, J. K., 2010. Dispersion, interfacial interaction and reagglomeration of functionalized carbon nanotubes in epoxy composites. Carbon, 48, 1824–1834.
Ma, P.-C., Siddiqui, N., Marom, G. & Kim, J.-K., 2010. Dispersion and functionalization of carbon nanotubes for polymer-based nanocomposites: A review. Composites, Part A , 41, 1345-1367.
Moore, D., 2004. The application of fracture mechanics to polymers, adhesives and composites. Amsterdam ; Oxford : Elsevier.
Pearson, R. A. & Yee, A. F., 1993. Toughening mechanisms in thermoplastics-modified epoxies.. Polymer, 34(17).
Petrie, E. M., 2006. Epoxy Adhesive Formulations. New York: McGraw Hill.
Pritchard, G. & Rhoades, G. V., 1976. The fracture of highly crosslinked resins. An invited review. Materials Science and Engineering, 26(1), 1-11.
Robert, B. et al., 2008. Nanostrength® Block Copolymers for Epoxy Toughening, Chicago, Illinois: Arkema Inc.
Sue, H.-J., Puckett, P. M., JL, B. & Walker, L., 2000. The network structure of epoxy systems and its relationship to toughness and toughenability. In: Pearson, Sue, Yee, editors. Toughening of plastics: Advances in modelling and experiments, 759.
Wetzel, B. et al., 2002. Impact and Wear Resistance of Polymer Nanocomposites at Low Filler Content,. Polym. Eng. Sci., 42(9), 1919-1927.
Wetzel, B., Haupert, F. & Zhang, M. Q., 2003. Epoxy nanocomposites with high mechanical and tribological performance. Compos. Sci. Technol, 63, 2055-2067.
Wetzel, B., Rosso, P., Haupert, F. & Friedrich, K., 2006. Epoxy nanocomposites – fracture and toughening mechanisms.. Engineering Fracture Mechanics, 73, 2375-2398.